

Specification No. 106807. Application No. 106807, dated 27th August, 1966. Complete specification left on 23rd June, 1967. (Application accepted 25th May, 1968.)

Index at acceptance—14D2[LVIII(1)].

PROVISIONAL SPECIFICATION.

A COMPOSITION FOR THE CATHODE FOR OXYGEN DEPOLARISATION.

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH, RAFI MARG, NEW DELHI-1, INDIA, AN INDIAN REGISTERED BODY INCORPORATED UNDER THE REGISTRATION OF SOCIETIES ACT (ACT XXI OF 1860).

THIS IS AN INVENTION BY DR. MICHAEL ANGELO VINCENT DEVANATHAN, SCIENTIST, CENTRAL ELECTROCHEMICAL RESEARCH INSTITUTE, KARAIKUDI-3, (CITIZEN OF CEYLON), SHRI VEERARAGHAVA ARAVAMUTHAN, SCIENTIST (CITIZEN OF INDIA), SHRI NARAYANAN RAMASAMY, SENIOR SCIENTIFIC ASSISTANT (CITIZEN OF INDIA) AND SHRI SRINIVASAN VENKATESAN, SENIOR LABORATORY ASSISTANT, (CITIZEN OF INDIA), ALL OF THE CENTRAL ELECTROCHEMICAL RESEARCH INSTITUTE, KARAIKUDI-3, MADRAS STATE.

The following specification describes the nature of this invention.

This invention relates to a New Manganese Dioxide Mix for Oxygen Depolarised Cathodes.

Hitherto it has been customary to use porous carbon cathodes in primary cells using caustic alkali, ammonium chloride and other neutral salt solutions as electrolyte and zinc, aluminium or magnesium as anode. This suffers from the disadvantage that only comparatively low, steady currents can be drawn.

The use of manganese dioxide as a depolariser with ammonium chloride or sodium hydroxide as electrolyte in primary cell systems hitherto has been making use of only the available oxygen of the manganese dioxide for depolarising purposes. This suffers from the disadvantage that the capacity of the cell is dependent entirely on the manganese dioxide content of the depolariser and the discharge characteristics of such systems shows a continuous fall of voltage even when used at low current drains.

The objective of this invention is to obviate these disadvantages by using a mixture of graphite or acetylene black or other conducting varieties of carbon and a suitable active form of manganese dioxide such as electrolytic or chemically precipitated or high grade ores and pressing to form a solid or hollow cathode dependent on the drain needed.

The following briefly describes the nature of the invention:

The cathode element is made by pressing a mixture of acetylene black or graphite or any conducting variety of carbon (5-25 per cent.) with a suitably active manganese dioxide and a binder that is unaffected by alkali and does not introduce high resistance to the block. The above mixture containing manganese dioxide and conducting carbon as ingredients is suitably mixed with a solution or emulsion of polymeric binder such as PVC, polypropylene, polyethylene, polystyrene, isoprene or rubber, polymethyl methacrylate, poly fluorocarbons such as teflon in solvents like carbon tetrachloride, trichloroethylene, benzene, toluene, chloroform or the like. This mixture is pressed to the desired shape of any size and geometry. It can be solid, hollow or perforated or combinations thereof with carbon or other suitable metallic current collectors. The solvent is allowed to evaporate either at the ambient temperature or at a slightly elevated temperature if it is required to accelerate the process.

Alternatively, the above manganese dioxide conducting carbon mix is mixed with the above-mentioned polymeric binders in finely powdered form and hot moulded to desired shapes.

The following examples illustrate the nature of the invention:

Example 1.

For high drains:

A manganese dioxide cathode made in the way described above using a peripheral metallic collector

and of hollow type or a flat disc type cathode when coupled with a zinc anode in alkaline solution is capable of delivering 2A continuous at a steady voltage of 1.2. The external dimensions of such a cathode are 8 cm. dia. and 16 cm. height. This is to be compared with AWC2 type cells that given only 1.1V at 1A continuous vide BS 1335. The ampere hour capacity of such a cell is limited solely by the zinc and the electrolyte. Over 1000 AH are normally realisable under such drain conditions with changed zinc and electrolyte.

Example 2.

For medium and low drains:

Cylindrical cathodes with zinc rod anodes and alkaline/ammonium chloride electrolyte can be used for comparatively low drains upto 1A continuous.

Example 3.

Dry cells:

Hollow cylindrical cathodes as in Example (1) can be fitted inside with a suitable anode and electrolyte paste assembly to make cells dimensionally equal to the well known dry cells e.g., No. 6, D type etc., but with higher capacity and flat discharge characteristics normally obtained only with HgO or Ag₂O depolarised cells.

Example 4.

Application to electrolytic cells:

In industrial electrolysis where hydrogen is a cathode product such as the chlor-alkali cell, electrolytic these cathodes, made in appreciably the same way manganese dioxide cells and the like as described earlier in cylinders or plates of suitable dimensions, can be used instead of the conventional iron or graphite cathodes. This has the advantage that the energy consumption is reduced by 0.5 to 0.8 V per cell.

The following are among the advantages of the invention:

1. Manganese dioxide available in India can be utilised. The cost of the cathode is low as cheaper manganese dioxide replaces comparatively expensive active carbon.
2. The performance of manganese dioxide air depolarised elements is superior to the conventional air depolarised cathodes (Example 1).
3. In the dry type of cells indicated in Example (4) one derives the advantage of getting a dead flat voltage plot achievable only in very costly miniature type mercuric

Price : TWO RUPEES.

oxide primary cells but using a cathode that is fabricated with very cheap material, i.e., manganese dioxide.

oxygen depolarised cathode which performs better than conventional carbon elements.

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Patent Officer,

Council of Scientific & Industrial Research.

Dated this 24th day of August, 1966.

Noteworthy feature :

A process whereby the catalytic activity of manganese dioxide has been utilised for the first time for

COMPLETE SPECIFICATION.

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The following specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed.

This invention relates to a composition for the cathode for oxygen depolarisation and has reference to a New Manganese Dioxide Mix for Oxygen Depolarised Cathodes.

Hitherto it has been customary to use porous carbon cathodes in primary cells using caustic alkali, ammonium chloride and other neutral salt solutions as electrolyte and zinc, aluminium or magnesium as anode. This suffers from the disadvantage that only comparatively low, steady currents can be drawn in the useful voltage range.

The use of manganese dioxide as a depolariser with ammonium chloride or sodium hydroxide as electrolyte in primary cell systems hitherto has been making use of only the available oxygen of the manganese dioxide for depolarising purposes. This suffers from the disadvantage that the capacity of the cell is dependent entirely on the manganese dioxide content of the depolariser and the discharge characteristics of such systems shows a continuous fall of voltage even when used at low current drains.

Hitherto it has been customary to use only metallic cathodes in industrial electrolytic cells where electro-oxidation or halogen evolution is the main reaction and hydrogen evolution at the cathode is permitted. This suffers from the disadvantage that the cell voltage is high due to cathodic reaction involving the evolution of hydrogen.

The object of this invention is to obviate these disadvantages.

According to the present invention, the composition for the cathode for oxygen depolarisation comprises a mixture of manganese dioxide powder and conducting variety of carbon (5 to 25 per cent.) such as acetylene black, graphite and a binder that is unaffected by alkali on electrolytic solution and does not introduce high resistance to the block.

Thus, the above referred difficulties have been obviated by using a manganese dioxide cathode fabricated as described below where the depolarisation is made independent of the quantity of the manganese dioxide and the current collection made independent of acetylene black or graphite by embodying the principle of matrix electrode covered in the patent No. 98157 (sealed).

The main findings of the invention consists in forming a cathode element by pressing a mixture of acetylene black or graphite or any conducting variety of carbon (5 to 25 per cent.) with a suitably active manganese dioxide and a binder that is unaffected by alkali on the electrolytic solution and does not introduce high resistance to the block. The above mixture containing manganese dioxide and conducting carbon

as ingredients is suitably mixed with a solution or emulsion of polymeric binder such as PVC, polypropylene, polyethylene, polystyrene, isoprene or rubber, polymethyl methacrylate, poly fluorocarbons such as teflon in solvents like carbon tetrachloride, trichloroethylene, benzene, toluene, chloroform, or the like. The mixture is pressed to the desired shape of any size and geometry. It can be solid, hollow or perforated or combinations thereof with carbon or other suitable metallic current collectors. The solvent is allowed to evaporate either at the ambient temperature or at a slightly elevated temperature if it is required to accelerate the process. Alternatively, the above manganese dioxide conducting carbon mix is mixed with the above-mentioned polymeric binders in finely powdered form and hot moulded to desired shapes.

This patent covers a process for the preparation of a new manganese dioxide mix for oxygen depolarised cathodes and its application in primary as well as in industrial electrolytic cells as a cathode in preference to conventional cathode use in the said applications.

To mention a typical example, the fabrication of the cathode for use in a typical primary wet cell may be considered. Taking the case of the cell that is equivalent to AW, BSS 1335 : 1946, a cylindrical metal matrix of 10 cm dia is used. This is suitably treated to resist alkali attack and pured with the mix of manganese dioxide and acetylene black, a quantity of about 300 g and the powder being used with any binder that is nonwetttable and non-reacting to have a block with density and packing of 2 to 3 g per cc. The details of the cell assembly and design are covered by our co-pending patent specification entitled "A new design for oxygen depolarised cells".

With the cathode of the above description is used in (a) primary cells in the way described in our co-pending patent specification entitled "A new design for oxygen depolarised cells" much higher current drains at improved voltages are possible. For example, cells using the outer containers of AW, cells covered by BSS 1335 : 1946, continuous current drain as high as one ampere can be obtained in a voltage range of 1.05 to 0.85 volts. This is to be compared with a drain of 150 milliamps continuous obtainable from a conventional cell covered by the above specifications. Using the same containers for sac 1 covered by IS 268 : 1955, the cell using this cathode can deliver a current of 120 milliamps for 1400 hours in the voltage range 1.25 to 1.1 volts whereas a corresponding range for a conventional cell is 1.4 to 0.85 volts. The following tables bring out clearly the advantages of the new system (Please see Tables I & II).

(b) In aqueous electrolysis, if the hydrogen evolution at the cathode is suppressed it will lead to an appreciable energy saving due to the reduction in cell voltage which can be as high as 30 per cent. in some cases due to depolarisation of hydrogen taking place at the cathode. Such a depolarisation effect is realised by employing this manganese dioxide cathode in industrial electrolytic cells thereby effecting a reduction in cell voltage of the order of 0.6 to 0.8 volt under identical conditions of electrolysis, the only change being the substitution of the conventional metal electrode by the new cathode elaborated in this patent. To cite one or two typical examples, in the conventional chloride to chlorate electro-oxidation using graphite anode and steel cathode, for a cathodic current density of 10 to 12 amp/sq.ft., the cell voltage as reported in literature is 2.6 to 2.8 volts. If the cathode is replaced by the manganese dioxide cathode described in the patent under the same conditions the cell voltage has been found to be 1.9 volts and at a cathodic current density of 30 amp/sq.ft., the cell voltage is 2.2 volts.

In the aqueous electrolysis of sodium chloride in a diaphragm cell using iron cathode and graphite anode at 40 amp/sq.ft., current density, the cell voltage is 3.4 volts as against a voltage of only 2.6 volts using the new cathode thus leading to an appreciable saving in energy under similar conditions.

The following are among the main advantages of the invention :

- (1) Very cheap and widely abundant manganese dioxide ores can be used for these cathodes ;
- (2) By virtue of the method of making and mechanism of action this system combines effectively the advantages of a manganese dioxide cathode with that of an oxygen depolarised cathode in aqueous electrolyte media, while also simultaneously conferring a sizeable reduction in quantity of depolariser required for realising far superior performance compared to conventional systems.

TABLE I.

Specification	BSS 1333 : 1946		IS 268 : 1955	
	New Cell	Conventional	New Cell	Conventional
Dimensions of container	As covered by the above specification		As covered by the above specification	
Anode	Zinc	Zinc	Zinc	Zinc
Cathode	MnO ₂	Porous carbon	MnO ₂	MnO ₂
Cathode area	75 sq. cm.	180 sq. cm.	40 sq. cm.	400 sq. cm.
Electrolyte	NaOH	NH ₄ Cl	NaOH	NH ₄ Cl
Current drain	1 amp. (max. continuous)	10 load (optimum)	10 load	10 load
Voltage range	1.0—0.85 at 1A	1.3—0.95	1.28—1.15	1.4 to 0.85
Life	300 A. H.	125 A. H.	1400 hrs.	1400 hrs.
Weight of cathode		200 gm.	200 gm.	2000 gm.

TABLE II.

Characteristics of a representative cell using the new manganese dioxide mix for oxygen depolarised cathode.

Cell dimensions correspond to cell outer dimensions of AW₁ cells of BSS 1335:1946.

	Cell with cathode having the new mix	Conventional cell as covered by BSS
Cathode area	75 sq. cm.	200 sq. cm.
Max. current density	14 mA/cm ² containing max.	2 mA/sq. cm. optimum
Ampere hour capacity per cycle of zinc and electrolyte	250—300 A. H.	125 A. H.
No. of cycles expected	4 (achieved) still active	3

We claim :

1. A composition for the cathode for oxygen depolarisation which comprises a mixture of manga-

nese dioxide powder and a conducting variety of carbon (5 to 25 per cent.) such as acetylene black, graphite and a binder that is unaffected by alkali or electrolytic solution and does not introduce high resistance to the block.

2. A composition as claimed in Claim 1 when used with the matrix type of electrode of patent No. 98157.

3. A composition as claimed in Claim 1 when used in the conventional way as in fabrication of normal cathodes.

4. A composition for the cathode for the oxygen depolarisation suitable for use in the matrix type of electrode of patent No. 98157 or similar electrodes for use as cathodes in electrolytic cells or in primary cells, substantially as hereinbefore described.

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Dated this 20th day of June, 1967.